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Excess Speed of Sound and Excess Molar Isentropic Compressibility in Binary Mixtures of Selected Amines in 2-Methoxy Ethanol at Various Temperatures

M. Narasaiah[a], K. Narendra[b], P. Bharath[c], T.S. Krishna[d] and D. Ramachandran[c,*]

[a]*Department of Chemistry, SKBR Government Degree College, Macherla 522426, Andhra Pradesh, India*
[b]*Department of Physics, V.R Siddhartha Engineering College, Vijayawada 520007, Andhra Pradesh, India*
[c]*Department of Chemistry, Acharya Nagarjuna University, Nagarjuna Nagar, 522510, Guntur, Andhra Pradesh, India*
[d]*Department of Physics, P.B Siddhartha College of Arts &Science, Vijayawada 520010, Andhra Pradesh, India*
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Speeds of sound and density of the mixtures were measured in the binary mixtures of 2-methoxy ethanol (2-ME) with selected amines (diethylamine (DEA), triethylamine (TEA), and tert-butylamine (TBA)) at 298.15, 303.15, 308.15, and 313.15 K at 0.1 MPa. We used the measured data to calculatethe excess speeds of sound, u^{E}, excess molar isentropic compressibility, and $K_{s,m}^{E}$.The computed quantities were fitted to the Redlich-Kister polynomial equation to derive the coefficients and estimate the standard error values. The excess speed of sound values varried from 18.41 ms^{-1} to 45.06 ms^{-1}, and the excess molar compressibility was in the range of -1.0270 × 10^{14} to -0.4070 × 10^{14} m^5 N^{-1} mol^{-1}, for all considered systems. The excess partial molar volume and isentropic compressibility of the constituents at infinite dilution were also calculated. According to our results, strong interactions were found between the selected alcohol and the molecules of aliphatic amines.

Key words: Speed of sound, Density, 2-Methoxyethanol, Amines, Intermolecular interactions

INTRODUCTION

The excess thermodynamic properties are very important to understand molecular interactions in binary fluid mixtures [1]. The information related to the properties of binary fluid mixtures in the chemical industry is vital in preparation, chemical separation, heat transfer, mass transfer, and fluid flow [2,3]. In our previous papers, we investigated the physicochemical and thermodynamic properties of binary mixtures of 2-methoxyethanol with organic solvents and ionic fluids at different temperatures [4-6]. The availability of oxy and hydroxyl groups in 2-methoxyethanol makes it a fascinating solvent; this is mainly due to formation of intra- and intermolecular hydrogen bonds between the -O- and -OH groups.

*Corresponding author. E-mail: dittakavirc@gmail.com

Significance of the H-bonding interactions between 2-ME and aliphatic amine molecules resulted in various applications for these materials in industry. In the present paper, densities, speeds of sound, excess molar isentropic compressibility, $K_{s,m}^{E}$ excess speed of sound, u^{E} and excess partial molar volumes $\bar{V}_{m,i}^{0E,\infty}$, and excess partial molar compressibilities $\bar{K}_{s,m,i}^{0E,\infty}$ at infinite dilution for the binary mixtures of 2-metoxyethanol with aliphatic amines at the temperatures of 298.15, 303.15, 308.15, and 313.15 K have been reported.

MATERIALS AND METHODS

2-ME and amines were provided from Sigma Aldrich, USA and were distilled [7,8]. Before tests, all these samples were dried for at least 72 h under a vacuum (≈0.1 Pa) at a moderate temperature. Fisher [9] titrator is used to evaluate

the final water content. The liquids are washed by distillation. After purification, the chemicals were >99 percent pure and were measured by the Gas Chromatography and also by measuring density/ultrasonic sound inquiry values with T = 298.15 to 313.15 K reported in [5,8,10-17]. The chemicals have been processed in amber dark bottles on molecular sieves of 0.4 nm. The literature comparison is listed in Table 1. The digital oscillating density and sound analyser (DSA 5000M, Anton Parr, Austria) with the reproducibility of $\pm 10^{-3}$ kg m^{-3} at density was tested with pure liquids and their binary mixture with $\pm 1 \times 10^{-2}$ ms^{-1} at the sound speed at 0.1 MPa. The densimeter dynamically modifies the viscosity with readings of up to 700 mPa. The sound speed was calculated by a 3 MHz frequency propagation time technique. The distilled water and anhydrous ethanol have been used after each calculation to purify the vibrating tube. The normal confidence instability in the current study is k = 1 (68 percent). Uncertainties in temperature, density, and speed were ±0.01 K, ±0.5 kg m^{-3} and ±0.8 m s^{-1}, respectively.

RESULTS

The experimental values of density and speed of sound of the mixtures in the temperature range from 298.15 to 313.15 K are presented in Table 2. The calculated values of

Table 1. Density, Speed of Sound, and Molar Heat Capacity Data at Different Temperatures at 0.1 MPa Obtained in this Work and from Available Literature Values

T (K)	ρ (g cm^{-3})		u (ms^{-1})		Cp (J K^{-1} mol^{-1})
	Expt	Ref.	Expt	Ref.	
2-ME					
298.15	0.9603	0.96032 [5]	1342.1	1342.1 [5]	176.40 [16]
303.15	0.9557	0.95571 [5]	1324.7	1324.7 [5]	177.76 [16]
308.15	0.9511	0.95108 [5]	1307.4	1307.4 [5]	179.12 [16]
313.15	0.9464	0.94642 [5]	1290.0	1290.1 [5]	180.48 [16]
Diethylamine					
298.15	0.6993	0.6993 [10]	1139.7	1344.5 [17]	169.34 [14]
		0.6989 [11]			
303.15	0.6940	0.6940 [10]	1115.7		169.44 [14]
		0.6939 [5]			
308.15	0.6887	0.6887 [10]	1091.8		
313.15	0.6833	0.6833 [10]	1067.8		
		0.6834 [8]			
Triethylamine					
298.15	0.7242	0.722892 [12]	1111.0	1111.2 [12]	216.43 [13]
303.15	0.7195	0.718332 [12]	1090.7	1091.1 [12]	
308.15	0.7148		1071.5		
313.15	0.7101		1053.5		
Tert-butylamine					
298.15	0.6907	0.69073 [15]	1068.4	1068.4[17]	
303.15	0.6857	0.68572 [15]	1050.0		
308.15	0.6806		1031.6		
313.15	0.6751		1013.2		

Standard uncertainties *s* are s(T) = ± 0.01 K, s(ρ) = ± 1 kg m^{-3}, s(u) = ± 0.8 ms^{-1}, and s(p) = ±1.0 kPa.

Table 2. Densities and Speeds of Sound as a Function of Mole Fraction of 2-ME at Different Temperatures

x_1	ρ (g cm^{-3})	u (ms^{-1})	ρ (g cm^{-3})	u (ms^{-1})	ρ (g cm^{-3})	u (ms^{-1})	ρ (g cm^{-3})	u (ms^{-1})
	298.15		303.15		308.15		313.15	
2-ME + DEA								
0.0000	0.6993	1139.7	0.6940	1115.8	0.6887	1091.8	0.6833	1067.9
0.1051	0.7267	1161.0	0.7215	1137.9	0.7163	1114.5	0.7110	1091.0
0.2088	0.7538	1182.0	0.7487	1160.4	0.7435	1137.8	0.7383	1114.0
0.2926	0.7757	1198.9	0.7706	1178.5	0.7655	1155.9	0.7603	1132.1
0.3807	0.7987	1216.8	0.7936	1197.4	0.7886	1175.0	0.7835	1151.1
0.5019	0.8303	1241.3	0.8254	1224.0	0.8204	1201.8	0.8154	1178.0
0.5925	0.8539	1259.6	0.8491	1243.0	0.8442	1222.0	0.8392	1198.5
0.6982	0.8815	1281.0	0.8767	1265.3	0.8719	1244.8	0.8670	1222.0
0.7862	0.9045	1298.8	0.8997	1283.0	0.8950	1263.5	0.8902	1241.5
0.8895	0.9315	1319.7	0.9268	1303.0	0.9221	1284.6	0.9173	1264.5
1.0000	0.9603	1342.1	0.9557	1324.7	0.9511	1307.4	0.9464	1290.1
2-ME + TEA								
0.0000	0.7242	1111.1	0.7195	1090.7	0.7148	1071.5	0.7101	1053.5
0.1040	0.7488	1135.1	0.7441	1115.0	0.7394	1096.0	0.7347	1078.1
0.2008	0.7716	1157.5	0.7670	1137.7	0.7623	1118.9	0.7576	1101.0
0.3020	0.7955	1180.9	0.7909	1161.4	0.7862	1142.7	0.7815	1124.9
0.3977	0.8181	1203.0	0.8135	1183.8	0.8088	1165.3	0.8041	1147.6
0.4919	0.8404	1224.7	0.8357	1205.8	0.8311	1187.5	0.8264	1169.9
0.6025	0.8665	1250.3	0.8618	1231.7	0.8572	1213.6	0.8525	1196.0
0.7018	0.8899	1273.2	0.8853	1254.9	0.8806	1237.0	0.8760	1219.5
0.7992	0.9129	1295.7	0.9083	1277.7	0.9036	1260.0	0.8990	1242.5
0.9095	0.9390	1321.2	0.9343	1303.5	0.9297	1286.0	0.9250	1268.6
1.0000	0.9603	1342.1	0.9557	1324.7	0.9511	1307.4	0.9464	1290.1
2-ME + tert-BA								
0.0000	0.6907	1068.4	0.6857	1050.0	0.6806	1031.6	0.6751	1013.2
0.1082	0.7199	1098.0	0.7149	1079.7	0.7098	1061.4	0.7045	1043.2
0.1908	0.7422	1120.6	0.7372	1102.4	0.7322	1084.2	0.7269	1066.0
0.2984	0.7712	1150.1	0.7663	1132.0	0.7613	1113.9	0.7561	1095.8
0.3982	0.7981	1177.4	0.7932	1159.4	0.7883	1141.4	0.7831	1123.4
0.5089	0.8279	1207.7	0.8231	1189.8	0.8182	1171.9	0.8132	1154.1
0.6109	0.8554	1235.6	0.8507	1217.8	0.8458	1200.1	0.8409	1182.3
0.6924	0.8774	1257.9	0.8727	1240.2	0.8679	1222.6	0.8630	1204.9
0.7833	0.9019	1282.8	0.8972	1265.2	0.8925	1247.6	0.8876	1230.1
0.9107	0.9362	1317.6	0.9316	1300.2	0.9269	1282.8	0.9222	1265.3
1.0000	0.9603	1342.1	0.9557	1324.7	0.9511	1307.4	0.9464	1290.1

Standard uncertainties, u, are $u(T) = \pm 0.02$ K; $u(\rho) = \pm 0.8$ kg m^{-3}; $u(u) = \pm 1$ ms^{-1}; $u(P) = \pm 0.002$ MPa, and $u(x) = \pm 1 \times 10^{-3}$.

Table 3. Excess Speed of Sound and Excess Molar Isentropic Compressibility as a Function of Mole Fraction, x_1, of 2-ME for 2-ME+ DEA Binary Mixtures at Different Temperatures

x_1	u^E (10^2 ms^{-1})	$K_{s,m}^E$ (10^{14} m^5 N^{-1} mol^{-1})	u^E (10^2 ms^{-1})	$K_{s,m}^E$ (10^{14} m^5 N^{-1} mol^{-1})
	298.15		303.15	
0.0000	0.0000	0.0000	0.0000	0.0000
0.1051	0.1888	-0.5255	0.1854	-0.5593
0.2088	0.3555	-0.8802	0.3550	-0.9432
0.2926	0.4729	-1.0637	0.4745	-1.1398
0.3807	0.5761	-1.1691	0.5790	-1.2499
0.5019	0.6756	-1.1843	0.6869	-1.2704
0.5925	0.7087	-1.1083	0.7188	-1.1836
0.6982	0.6879	-0.9348	0.6994	-0.9974
0.7862	0.6054	-0.7264	0.6119	-0.7704
0.8895	0.4031	-0.4129	0.4002	-0.4317
1.0000	0.0000	0.0000	0.0000	0.0000
	308.15		313.15	
0.0000	0.0000	0.0000	0.0000	0.0000
0.1051	0.1905	-0.6154	0.2006	-0.6901
0.2088	0.3682	-1.0423	0.3800	-1.1538
0.2926	0.4866	-1.2490	0.5021	-1.3819
0.3807	0.5920	-1.3654	0.6102	-1.5089
0.5019	0.6995	-1.3813	0.7205	-1.5242
0.5925	0.7401	-1.2940	0.7636	-1.4278
0.6982	0.7199	-1.0875	0.7455	-1.2002
0.7862	0.6344	-0.8422	0.6591	-0.9291
0.8895	0.4182	-0.4729	0.4398	-0.5236
1.0000	0.0000	0.0000	0.0000	0.0000

$K_{s,m}^E$ and u^E for the three mixtures at different temperatures are presented in Tables 3-5.

Excess Properties

Douheret *et al.* [18] used the relations to calculate the excess molar isentropic compressibility

$$K_{s,m}^E = K_{s,m} - K_{s,m}^{id} \quad (1)$$

where $K_{s,m}^{id}$ is the molar isentropic compressibility of the ideal mixture. $K_{s,m}^{id}$ values for binary mixtures were calculated as suggested by Benson and Kiyohara [19]:

$$K_{S,m}^{id} = x_1 K_{s,m,1} + x_2 K_{s,m,2} + T\left[\frac{x_1\left(V_{m,1}\alpha_{p,1}\right)^2}{C_{p,1}} + \frac{x_2\left(V_{m,2}\alpha_{p,2}\right)^2}{C_{p,2}} - \frac{\left(V_m^{id}\alpha_p^{id}\right)^2}{C_p^{id}}\right] \quad (2)$$

where, V_m, α_p and C_p are molar volume, isobaric expansivity and molar heat capacity respectively. V_m^{id}, α_p^{id} and C_p^{id} are calculated using the following relations:

$$V_m^{id} = x_1 V_{m,1} + x_2 V_{m,2} \quad (3)$$

$$\alpha_p^{id} = \phi_1 \alpha_{p,1} + \phi_2 \alpha_{p,2} \quad (4)$$

$$C_p^{id} = x_1 C_{p,1} + x_2 C_{p,2} \quad (5)$$

Table 4. Excess Speed of Sound and Excess Molar Isentropic Compressibility as a Function of Mole Fraction, x_1, of 2-ME for 2-ME+ TEA Binary Mixtures at Different Temperatures

x_1	u^E (10^2 ms^{-1})	$K_{s,m}^E$ (10^{14} m^5 N^{-1} mol^{-1})	u^E (10^2 ms^{-1})	$K_{s,m}^E$ (10^{14} m^5 N^{-1} mol^{-1})
	298.15		303.15	
0.0000	0.0000	0.0000	0.0000	0.0000
0.1040	0.1841	-0.8368	0.1868	-0.8985
0.2008	0.3422	-1.3630	0.3474	-1.4623
0.3020	0.4899	-1.6929	0.4977	-1.8147
0.3977	0.6083	-1.8281	0.6183	-1.9584
0.4919	0.6979	-1.8174	0.7098	-1.9456
0.6025	0.7566	-1.6489	0.7703	-1.7641
0.7018	0.7490	-1.3743	0.7633	-1.4695
0.7992	0.6598	-1.0079	0.6734	-1.0771
0.9095	0.4065	-0.4922	0.4158	-0.5258
1.0000	0.0000	0.0000	0.0000	0.0000
	308.15		313.15	
0.0000	0.0000	0.0000	0.0000	0.0000
0.1040	0.1888	-0.9610	0.1898	-1.0230
0.2008	0.3513	-1.5629	0.3531	-1.6627
0.3020	0.5034	-1.9383	0.5062	-2.0608
0.3977	0.6256	-2.0905	0.6294	-2.2214
0.4919	0.7187	-2.0758	0.7234	-2.2047
0.6025	0.7806	-1.8811	0.7862	-1.9967
0.7018	0.7744	-1.5662	0.7806	-1.6617
0.7992	0.6841	-1.1475	0.6904	-1.2170
0.9095	0.4233	-0.5599	0.4279	-0.5935
1.0000	0.0000	0.0000	0.0000	0.0000

Table 5. Excess Speed of Sound and Excess Molar Isentropic Compressibility as a Function of Mole Fraction, x_1, of 2-ME for 2-ME+ tert-BA Binary Mixtures at Different Temperatures

x_1	u^E (10^2 ms^{-1})	$K_{s,m}^E$ (10^{14} m^5 N^{-1} mol^{-1})	u^E (10^2 ms^{-1})	$K_{s,m}^E$ (10^{14} m^5 N^{-1} mol^{-1})
	298.15		303.15	
0.0000	0.0000	0.0000	0.0000	0.0000
0.1082	0.2269	-0.7339	0.2293	-0.7888
0.1908	0.3839	-1.1159	0.3882	-1.1988
0.2984	0.5628	-1.4204	0.5694	-1.5250
0.3982	0.6966	-1.5376	0.7055	-1.6502
0.5089	0.7989	-1.5121	0.8100	-1.6220
0.6109	0.8369	-1.3660	0.8496	-1.4648
0.6924	0.8162	-1.1766	0.8296	-1.2614
0.7833	0.7221	-0.8989	0.7352	-0.9635
0.9107	0.4097	-0.4070	0.4184	-0.4362
1.0000	0.0000	0.0000	0.0000	0.0000
	308.15		313.15	
0.0000	0.0000	0.0000	0.0000	0.0000
0.1082	0.2329	-0.8524	0.2389	-0.9302
0.1908	0.3945	-1.2950	0.4050	-1.4134
0.2984	0.5793	-1.6469	0.5957	-1.7980
0.3982	0.7185	-1.7817	0.7399	-1.9459
0.5089	0.8261	-1.7511	0.8525	-1.9137
0.6109	0.8679	-1.5813	0.8977	-1.7294
0.6924	0.8489	-1.3619	0.8800	-1.4903
0.7833	0.7539	-1.0404	0.7840	-1.1394
0.9107	0.4308	-0.4711	0.4506	-0.5167
1.0000	0.0000	0.0000	0.0000	0.0000

α_p values were calculated from the temperature dependence of the density data of pure liquids by using the Equation:

$$\alpha_p = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p = -\left(\frac{\partial \ln \rho}{\partial T}\right)_p \quad (6)$$

In the present work, DEA and TBA with 2-ME, α_p values can be obtain from a linear dependence of ρ with T. In the case of TEA with 2-ME, these are nonlinear. The estimated uncertainty in α_p is within ±0.003 kK^{-1}.The excess speed of sound can be computed by the Equation:

$$u^E = u - u^{id} \quad (7)$$

Douheret et al. computed the speed of sound in an ideal-mixture using Equation:

$$u^{id} = \left(\frac{V_m^{id}}{\kappa_s^{id} M}\right)^{1/2} \quad (8)$$

The excess values of the above parameters for the mixtures have been fitted to the Redlich-Kister [20] polynomial Equation:

$$Y^E = x_1 x_2 \sum_{i=0}^{j} A_i (2x_1 - 1)^i \quad (9)$$

where Y^E is $K_{s,m}^E$ and u^E. The coefficients, A_i, obtained by the method of least squares with equal weights assigned to each point were calculated along with the standard deviation σ (Y^E). The coefficients were adjustable parameters for a better fit of the excess functions.

The standard deviation $\sigma(Y^E)$ is calculated using the following Equation:

$$\sigma(Y^E) = \left(\frac{\sum (Y_{expt}^E - Y_{cal}^E)^2}{(m - n)}\right)^{1/2} \quad (10)$$

Where m equals to the number of experimental points, n is the number of A_i coefficients considered (n + 1 in the present study). The optimal number of A_i coefficients has been determined statistically by performing F-test. The coefficients, A_i, and corresponding standard deviations, σ fit of $K_{s,m}^E$, u^E, Standard error (σ), and standard deviation are reported in Table 6. The variations of $K_{s,m}^E$ and u^E, with mole fraction x_1 along with smoothed values from Eq. (9) at studied temperatures are shown graphically in Fig. 1 and Fig. 2, respectively."

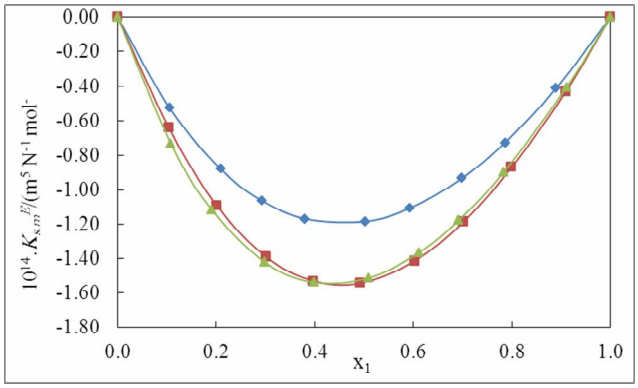

Fig. 1. Excess molar isentropic compressibilities ($K_{s,m}^E$) with mole fraction x_1 of 2-ME in the binary mixtures of 2-ME (1) with amines (2); (♦), DEA; (■), TEA; (▲), Tert-BA; at temperature 298.15 K. The points represent experimental values and solid lines have been drawn from Eq. (9) using the coefficients given in Table 6.

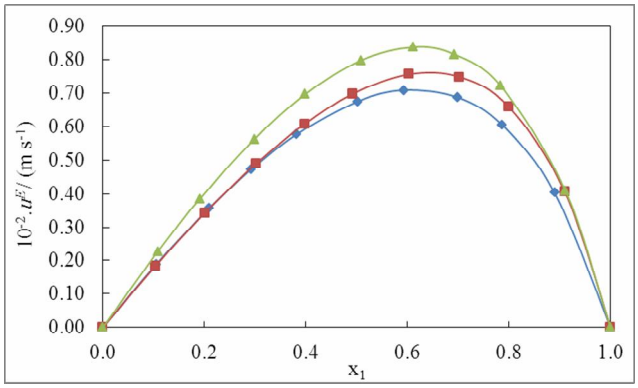

Fig. 2. Excess speed of sound (u^E) with mole fraction x_1 of 2-ME in the binary mixtures of 2-ME (1) with amines (2); (♦), DEA; (■), TEA; (▲), Tert-BA; at temperature 298.15 K. The points represent experimental values and solid lines have been drawn from Equation (9) using the coefficients given in Table 6.

Table 6. Coefficients A_j of Eq. (9) along with Standard Deviations σ of Binary Mixture Properties

Parameter	T (K)	A_0	A_1	A_2	σ
2-ME + DEA					
$K_{s,m}^{E}$ (10^{14} m^5 N^{-1} mol^{-1})	298.15	-4.7404	0.8685	-0.2403	0.0006
	303.15	-5.0784	0.9658	-0.1637	0.0023
	308.15	-5.5374	1.0904	-0.2806	0.0040
	313.15	-6.1082	1.2325	-0.3857	0.0040
u^{E} (10^2 ms^{-1})	298.15	2.6942	1.2601	0.5825	0.0040
	303.15	2.7351	1.2973	0.4887	0.0025
	308.15	2.7969	1.3572	0.6020	0.0033
	313.15	2.8790	1.4218	0.7113	0.0035
2-ME + TEA					
$\kappa_{s,m}^{E}$ (10^{14} m^5 N^{-1} mol^{-1})	298.15	-6.1524	1.1266	0.1095	0.0042
	303.15	-6.6102	1.2371	0.1023	0.0044
	308.15	-7.0731	1.3470	0.0952	0.0046
	313.15	-7.5284	1.4561	0.0908	0.0049
u^{E} (10^2 ms^{-1})	298.15	2.8093	1.6449	0.9003	0.0078
	303.15	2.8573	1.6881	0.9315	0.0082
	308.15	2.8929	1.7236	0.9601	0.0085
	313.15	2.9116	1.7463	0.9795	0.0088
2-ME + tert-BA					
$\kappa_{s,m}^{E}$ (10^{14} m^5 N^{-1} mol^{-1})	298.15	-6.0780	1.6068	-0.4029	0.0014
	303.15	-6.5201	1.7365	-0.4408	0.0015
	308.15	-7.0390	1.8777	-0.4847	0.0017
	313.15	-7.6921	2.0293	-0.5362	0.0018
u^{E} (10^2 ms^{-1})	298.15	3.1647	1.5235	0.7257	0.0057
	303.15	3.2080	1.5667	0.7565	0.0060
	308.15	3.2710	1.6270	0.7996	0.0064
	313.15	3.3741	1.7218	0.8664	0.0071

Partial Molar Properties

The partial molar properties (partial molar volume and partial molar compressibility), $\overline{Y}_{m,1}$ of component 1 (2-ME) and $\overline{Y}_{m,2}$ of component 2 (amines), in these mixtures over entire composition range were calculated by using the following Equations

$$\overline{Y}_{m,1} = Y_m^E + Y_{m,1}^* + x_2\left(\frac{\partial Y_m^E}{\partial x_1}\right)_{T,p} \quad (11)$$

$$\overline{Y}_{m,2} = Y_m^E + Y_{m,2}^* + x_1\left(\frac{\partial Y_m^E}{\partial x_1}\right)_{T,p} \quad (12)$$

where Y is V or K_s, $Y_{m,1}^*$ and $Y_{m,2}^*$ are the molar properties for pure components 2-ME and amines, respectively. The derivative, $(\partial Y^E/\partial x_1)_{T,p}$ in Eqs. (11) and (12) was obtained by differentiation of the Eq. (11), which leads to the following equations for $\overline{Y}_{m,1}$ and $\overline{Y}_{m,2}$

$$\overline{Y}_{m,1} = Y_{m,1}^* + x_2^2\sum_{i=0}^{n} A_i(2x_1-1)^i - 2x_1x_2^2\sum_{i=1}^{n} A_i(2x_1-1)^{i-1} \quad (13)$$

$$\overline{Y}_{m,2} = Y_{m,2}^* - x_1^2\sum_{i=0}^{n} A_i(1-2x_1)^i + 2x_1^2x_2\sum_{i=1}^{n} A_i(1-2x_1)^{i-1} \quad (14)$$

The excess partial molar properties were calculated by the following relations [21,22]:

$$\overline{Y}_{m,i}^{E} = Y_{m}^{E} + (1 - x_1)\left(\partial Y_{m}^{E} \Big/ \partial x_i\right) \quad (15)$$

We are interested to evaluate the partial molar properties of 2-ME at infinite dilution ($x_1 = 0$) in aliphatic amines, and the partial molar properties of amines at infinite dilution ($x_2 = 0$) in 2-ME. Therefore, $\overline{Y}_{m,1}^{\circ}$ is obtained by setting $x_1 = 0$ which leads to

$$\overline{Y}_{m,1}^{0} = Y_{m,1}^{*} + \sum_{i=0}^{n} A_i (-1)^i \quad (16)$$

Similarly by setting $x_2 = 0$, tone can obtain:

$$\overline{Y}_{m,2}^{0} = Y_{m,2}^{*} + \sum_{i=0}^{n} A_i \quad (17)$$

here $\overline{Y}_{m,1}^{\circ}$ and $\overline{Y}_{m,2}^{\circ}$ represent the partial molar properties of 2-ME at infinite dilution in amines and the partial molar properties of amines at infinite dilution in 2-ME, respectively.

Excess partial molar properties at infinite dilution $\overline{Y}_{m,i}^{\circ,E}$ for each component in binary liquid mixtures were evaluated through relations

$$\overline{Y}_{m,1}^{0,E} = \overline{Y}_{m,1}^{0} - Y_{m,1}^{*} \quad (18)$$

$$\overline{Y}_{m,2}^{0,E} = \overline{Y}_{m,2}^{0} - Y_{m,2}^{*} \quad (19)$$

The values of $\overline{V}_{\mathrm{m},1}^{\circ}$, $V_{\mathrm{m},1}^{*}$, $\overline{V}_{\mathrm{m},1}^{\circ\mathrm{E}}$, $\overline{V}_{\mathrm{m},2}^{\circ}$, $V_{\mathrm{m},2}^{*}$ and $\overline{V}_{\mathrm{m},2}^{\circ\mathrm{E}}$; and $\overline{K}_{\mathrm{s,m},1}^{\circ}$, $K_{\mathrm{s,m},1}^{*}$, $\overline{K}_{\mathrm{s,m},1}^{\circ\mathrm{E}}$, $\overline{K}_{\mathrm{s,m},2}^{\circ}$, $K_{\mathrm{s,m},2}^{*}$ and $\overline{K}_{\mathrm{s,m},2}^{\circ\mathrm{E}}$ for the binary mixtures are listed in Tables 7 and 8, respectively.

DISCUSSION

Excess molar isentropic compressibility ($K_{s,m}^{E}$) data for the 2-ME mixtures with aliphatic amines are shown graphically in Fig. 1 and the data are given in Tables 3-5. For all binary systems, these values were negative at 298.1 313.15 K and atmospheric pressure over the entire composition spectrum.

Table 7. The Values $\overline{V}_{\mathrm{m},1}^{\circ}$, $V_{\mathrm{m},1}^{*}$, $\overline{V}_{\mathrm{m},1}^{\circ\mathrm{E}}$, $\overline{V}_{\mathrm{m},2}^{\circ}$, $V_{\mathrm{m},2}^{*}$ and $\overline{V}_{\mathrm{m},2}^{\circ\mathrm{E}}$ of the Components for 2-ME + Amines Mixtures at Different Temperatures from Redlich-Kister Equation

T (K)	$10^6 \times \overline{V}_{\mathrm{m},1}^{\circ}$ ($m^3\ mol^{-1}$)	$10^6 \times V_{\mathrm{m},1}^{*}$	$10^6 \times \overline{V}_{\mathrm{m},1}^{\circ\mathrm{E}}$	$10^6 \times \overline{V}_{\mathrm{m},2}^{\circ}$	$10^6 \times V_{\mathrm{m},2}^{*}$	$10^6 \times \overline{V}_{\mathrm{m},2}^{\circ\mathrm{E}}$
2-ME + DEA						
298.15	69.791	79.234	-9.443	97.677	104.590	-6.913
303.15	69.920	79.616	-9.696	98.310	105.389	-7.079
308.15	70.048	80.004	-9.956	98.951	106.200	-7.249
313.15	70.165	80.398	-10.233	99.609	107.039	-7.430
2-ME + TEA						
298.15	80.463	79.234	1.229	121.571	139.725	-18.154
303.15	70.179	79.616	-9.437	132.841	140.632	-7.790
308.15	69.166	80.004	-10.838	134.853	141.556	-6.704
313.15	70.995	80.398	-9.403	134.038	142.501	-8.463
2-ME + tert-BA						
298.15	68.859	79.234	-10.375	98.381	105.888	-7.507
303.15	68.998	79.616	-10.619	98.997	106.662	-7.665
308.15	69.117	80.004	-10.887	99.632	107.470	-7.838
313.15	69.202	80.398	-11.195	100.301	108.338	-8.037

Table 8. The Values $\overline{K}^{\circ}_{s,m,1}$, $K^{*}_{s,m,1}$, $\overline{K}^{\circ E}_{s,m,1}$, $\overline{K}^{\circ}_{s,m,2}$, $K^{*}_{s,m,2}$ and $\overline{K}^{\circ E}_{s,m,2}$ of the Components for 2-ME + Amines Binary Mixtures at Different Temperatures

T (K)	$10^{14} \times \overline{K}^{\circ}_{s,m,1}$ ($m^5\ N^{-1}\ mol^{-1}$)	$10^{14} \times K^{*}_{s,m,1}$	$10^{14} \times \overline{K}^{\circ E}_{s,m,1}$	$10^{14} \times \overline{K}^{\circ}_{s,m,2}$	$10^{14} \times K^{*}_{s,m,2}$	$10^{14} \times \overline{K}^{\circ E}_{s,m,2}$
2-ME + DEA						
298.15	-4.862	4.581	-9.443	4.602	11.515	-6.913
303.15	-4.949	4.747	-9.696	5.120	12.198	-7.079
308.15	-5.035	4.921	-9.956	5.687	12.936	-7.249
313.15	-5.129	5.104	-10.233	6.307	13.738	-7.430
2-ME + TEA						
298.15	5.809	4.581	1.229	-2.526	15.628	-18.154
303.15	-4.690	4.747	-9.437	8.639	16.429	-7.790
308.15	-5.917	4.921	-10.838	10.544	17.248	-6.704
313.15	-4.298	5.104	-9.403	9.618	18.081	-8.463
2-ME + tert-BA						
298.15	-5.794	4.581	-10.375	5.923	13.430	-7.507
303.15	-5.871	4.747	-10.619	6.444	14.109	-7.665
308.15	-5.965	4.921	-10.887	7.001	14.839	-7.838
313.15	-6.091	5.104	-11.195	7.595	15.632	-8.037

According to Kiyohara and Benson [23], $K^{E}_{s,m}$ is the sum of a variety of opposing effects:

(i) If free-length increases, the probability of dipolar association breakdown, H-bond rupture, and size and shape disparity between pure component molecules may all contribute to a decrease in the speed of sound.

(ii) When dipole-dipole, H-bonding, and complex formation between the component molecules cause a reduction in free-length, this may lead to an increase in the speed of sound in mixtures compared to pure components. The former effect explains the negative deviation and the later effect leads to a positive deviation in κ^{E}_{s} [24]. The magnitude of the various contributions depends mainly on the relative molecular size of the components.

The negative values of $K^{E}_{s,m}$ of the liquid mixture are less compressible than those of pure liquids and show that the molecules in the mixture are more closely bound than those in the pure liquids. This corroborates the existence, probably through hydrogen bonding [25] between different molecules, of relatively stronger donor-acceptor interaction.

Figure 2 shows that over the entire mole fraction range, u^{E} values are positive for 2-ME with amines. It is common that positive deviations suggest strong interactions, while negative deviations show a lack of such interactions.

For the three binary mixtures over the entire composition range, a perusal of Fig. 3 and Fig. 4 shows that

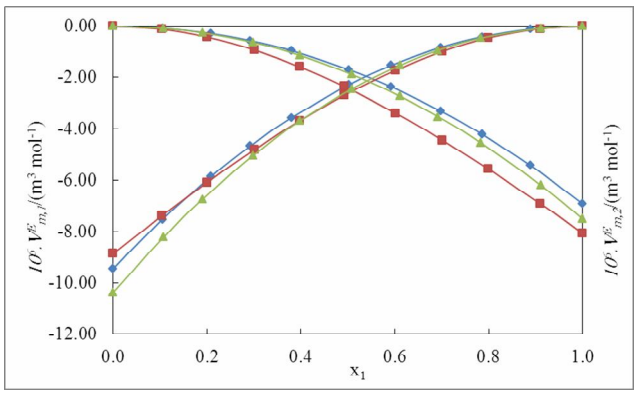

Fig. 3. Excess partial molar volume ($\overline{V}^{E}_{m,1}$ and $\overline{V}^{E}_{m,2}$) with mole fraction x_1 of 2-ME in the binary mixtures of 2-ME (1) with amines (2); (♦), DEA; (■), TEA; (▲), Tert-BA; at temperature 298.15 K.

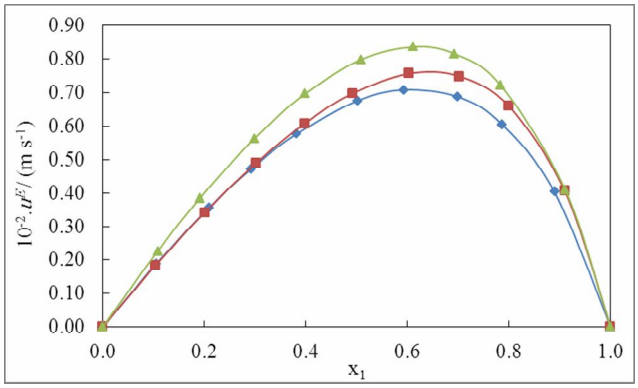

Fig. 4. Excess partial molar compressibilities ($\overline{K}^{E}_{s,m,1}$ and $\overline{K}^{E}_{s,m,2}$) with mole fraction x_1 of 2-ME in the binary mixtures of 2-ME (1) with amines (2); (♦), DEA; (■), TEA; (▲), Tert-BA; at temperature 298.15 K

the values of $\overline{V}^{E}_{m,1}$ and $\overline{V}^{E}_{m,2}$; $\overline{K}^{E}_{s,m,1}$ and $\overline{K}^{E}_{s,m,2}$ are negative. This means that in the pure state, the molar volumes or molar isentropic compressibilities of every constituent in the blend are lower than their particular molar volume or molar isentropic compressibilities, *i.e.* there is a diminish in volumeor isentropic compressibilities when 2-ME is combined with amines. In general, negative $\overline{V}^{E}_{m,1}$ and $\overline{V}^{E}_{m,2}$; $\overline{K}^{E}_{s,m,1}$ and $\overline{K}^{E}_{s,m,2}$ values indicate that there are major solvent-solute interactions between different molecules, while positive $\overline{V}^{E}_{m,1}$ and $\overline{V}^{E}_{m,2}$; $\overline{K}^{E}_{s,m,1}$ and $\overline{K}^{E}_{s,m,2}$ values indicate that there are weak interactions in the mixture. The negative $\overline{V}^{E}_{m,1}$ and $\overline{V}^{E}_{m,2}$; $\overline{K}^{E}_{s,m,1}$ and $\overline{K}^{E}_{s,m,2}$ values show that 2-ME interactions with aliphatic amines are greater than interactions between similar molecules that lead to volume and compressibility decreases.

Table 7 and Table 8 show that at each tested temperature, the values of $\overline{V}^{\circ E}_{m,1}$ and $\overline{V}^{\circ E}_{m,2}$; $\overline{K}^{\circ E}_{s,m,1}$ and $\overline{K}^{\circ E}_{s,m,2}$ are negative for these binary systems. This means that the $K_{s,m}$ in each portion in the mixture is less than the $K_{s,m}$ in the pure state, *i.e.* there is a volume contraction or decrease in the mixing with aliphatic amines of 2-ME. The observed negatives values of $\overline{V}^{\circ E}_{m,1}$ and $\overline{V}^{\circ E}_{m,2}$ suggest that 2-ME interactions with aliphatic amines are greater than interactions between similar molecules.

The values of $\overline{V}^{\circ E}_{m,1}$ and $\overline{V}^{\circ E}_{m,2}$; $\overline{K}^{\circ E}_{s,m,1}$ and $\overline{K}^{\circ E}_{s,m,2}$ as proposed by Hawrylak *et al.* [26] and Rodham *et al.* [27], can be evaluated in terms of structural and geometrical compressibility. Structural compressibility results from the breakdown of the related structure (owing to complicated interactions between 2-ME and aliphatic amine molecules), and geometric compressibility results from the simultaneous compression of the molecules (due to complex interactions between 2-ME and aliphatic amine molecules), lead to a volume contraction and a decrease in compressibility. The observed values of $\overline{V}^{\circ E}_{m,1}$ and $\overline{V}^{\circ E}_{m,2}$; $\overline{K}^{\circ E}_{s,m,1}$ and $\overline{K}^{\circ E}_{s,m,2}$ suggest that the geometric compressibility is a dominant factor in these mixtures. The patterns observed in $K^{E}_{s,m}$ and u^{E} values are also supported by $\overline{V}^{\circ E}_{m,1}$ and $\overline{V}^{\circ E}_{m,2}$; $\overline{K}^{\circ E}_{s,m,1}$ and $\overline{K}^{\circ E}_{s,m,2}$ values.

CONCLUSIONS

The densitiy and speeds of sound of binary mixtures of 2-methoxy ethanol with aliphatic amines namely diethylamine, triethylamine, and tert-butylamine were measured at 298.15-313.15 K at an interval of 5 K. From the experimental data, excess isentropic compressibility and excess speed of sound; $\overline{V}_{m,1}$ and $\overline{V}_{m,2}$; $\overline{V}^{E}_{m,1}$ and $\overline{V}^{E}_{m,2}$; $\overline{K}_{s,m,1}$ and $\overline{K}_{s,m,2}$; $\overline{K}^{E}_{s,m,1}$ and $\overline{K}^{E}_{s,m,2}$ of the components over the whole composition range, and excess partial molar volumes and isentropic compressibilities of the constituents at infinite dilution were calculated. The trends in the changes of these parameters shows the interactions between the molecules. The values of excess isentropic compressibility and excess speed of sound were fitted to Redlich-Kister polynomial equation. The consoldation of all the results and information derived from them indicate that strong interactions exist between the selected alcohol and the molecules of aliphatic amines.

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